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(54) Title: METHOD FOR MAKING AND USING PLATINIZED MICROPOROUS CERAMIC MATERIALS

(57) Abstract

A method for platinizing microporous nanoparticulate ceramic metal oxide materials having a high surface area and mean pore diameter less than 100 Å produces a platinized catalyst suitable for degradation of organic compounds in the gas phase. The platinized catalyst produced according to the method retains the advantageous properties of the starting materials and exhibits greater catalytic activity than existing platinized metal oxide catalysts. The materials have a characteristic dark black color, in contrast to the gray materials known to the art, suggesting improved platinum loading.

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METHOD FOR MAKING AND USING
PLATINIZED MICROPOROUS CERAMIC MATERIALS

Field of the Invention
        The present invention relates to the field of
10   microporous nanoparticulate ceramic catalysts and more
      particularly to a method for making and using
      platinized microporous nanoparticulate ceramic
      catalysts.

Background of the Invention
15   Contamination of ground water and soils by
      volatile organic compounds associated with fuel leaks
      and improper solvent disposal is a widespread
      environmental problem. One promising remedial
      approach is to use semiconductor-mediated heterogenous
20   photocatalytic oxidation to destroy such volatile
      organic compounds. Heterogenous photocatalytic
      oxidation is also used for synthesis and in catalytic
      converters in automobiles.
        Initial research in this area focused largely on
25   volatile aliphatic halogenated organic compounds such
      as TCE and PCE. Several photocatalysts have been
      developed which are able, under well defined
      conditions, to achieve complete, or nearly complete,
      mineralization of such compounds.
30   Recently, attention has shifted to the more
      difficult to degrade compounds, particularly aromatic
      compounds such as benzen , chlorobenzene, toluene,

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phenol, chlorophenols, and benzoic acid. Typically,
the catalysts employed in efforts to remediate
contamination by aromatics are heterogeneous photo-
assisted catalysts in the form of semiconductor
5   powders dissolved in aqueous suspension. Titanium
dioxide powders (e.g., Degussa P25) are the most
widely used heterogeneous catalysts for
photocatalytically oxidizing aromatic compounds. When
a suspension of titanium dioxide powder is illuminated
10   with UV light, many aromatic compounds are converted
to other compounds. In some cases, complete
mineralization of the aromatic compound to carbon
dioxide and water has been achieved in the gas phase
under conditions of high temperature and long reaction
15   time.

One way to increase the efficiency of titania
photocatalysis is to provide a catalytic metal,
generally platinum, at the surface of the titania
material. Existing platinized titania catalysts are
20   titania powders (particle size 125 microns-150
microns) with platinum in the range of 0.5-10% by
weight. Using certain platinized titania materials as
photocatalysts, photodecomposition of aqueous
solutions of benzene to carbon dioxide as the final
25   product, with several other minor by-products has been
reported.

However, there is much room for improvement in
both the catalytic materials and the catalytic
photodegrading processes for complex organic
30   compounds, both aromatic and aliphatic. One
shortcoming of existing systems is that complete
mineralization requires relatively long reaction
times. In addition, a filtration process is required
after a liquid phase reaction is complete to separate
35   the solid photocatalyst powder from the reaction
mixture. Perhaps the most challenging problem, as a
practical matter, is the need to balance the desire

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for maximum catalytic efficiency against the high cost
of platinum metal.

Thus, it would be desirable to obtain a
photocatalyst that operates efficiently using only
5   minimal amounts of platinum that can be incorporated
into a method for removing organic compounds that is
rapid and does not require post-reaction separation of
catalytic material.

There is also room for improvement in the
10   processes for preparing efficient platinized metal
oxide photocatalysts. Kraeutler and Bard, J. M. Chem.
Soc., 100:4317-4318 (1978) described photodepositing
metallic platinum on 125-150 micron particle size
anatase powder. The anatase powder was suspended in
15   hexachloroplatinic acid at pH 4, flushed with nitrogen
to remove oxygen and CO_2, and heated to about 55°C.
Photodeposition of the platinum was achieved by
irradiating the reaction mixture using an Hg-Xe lamp
for 3.6 hours. The resulting platinized titania
20   powder was described as being significantly darker
than the grayish anatase powder. The distribution of
platinum on the resulting material was described as
fairly uniform and no agglomerates were detected by
SEM. However, Kraeutler and Bard went on to note that
25   metal deposition probably only occurs near sites where
photons strike the surface and the light flux can be
made very small. Thus, one would expect to find small
clusters of the metal on the external support surface.
Moreover, this process requires high temperature
30   treatment to disperse the platinum on the surface
without forming large aggregates. Also, the system
deposits on the reactor wall in the path of incident
light, resulting in waste and unnecessary expense.
Platinum so deposited can ultimately largely prevent
35   light from reaching the catalyst, further reducing the
deposition efficiency.

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Izumi et al., later characterized the titania
powders platinized by Kraeutler and Bard as containing
10% platinum by weight, which would suggest a
prohibitively high cost for the catalyst in a
5   commercial setting. Izumi et al. demonstrated
photocatalytic decomposition of benzene and aliphatic
hydrocarbons in the liquid phase using these
materials. Later, Izumi et al. reported the use of
the same platinized titania powders to photo-oxidize
10   benzoic acid and to photocatalytically decompose
adipic acid, also in the liquid phase.

A second method used to deposit platinum on a
titania powder uses high-temperature reduction of a
platinum precursor in H_2 gas. In this method,
15   described by Pichat et al., Nouv. J. de Chim., 5:627-
636 (1981), non-porous anatase powder (50 m^2/g (Degussa
P25) is suspended in a small amount of distilled water
with hexachloroplatinic acid, evacuated in a rotating
flask at 350° K for 2 hours, dried at 393° K for 2
20   hours, flushed with N_2 while raising the temperature to
573° K, reduced in hydrogen gas at 753° K for 15
hours. Finally, the powder is cooled in a nitrogen
stream. The platinized titania powders produced by
Pichat, et al. were reported to be 4.85% platinum by
25   weight. The authors also reported good homodispersion
and a platinum particle size of 2-2.5 nanometers, with
some 1 nanometer and 3 nanometer particles also
observed. These catalysts were then used in both
liquid phase and gas phase reactions. However, in the
30   gas phase, only a simple alcohol (methanol) was
degraded.

Sato, J. Catal., 92:11-16 (1985) reported a
photoelectrochemical platinization method wherein
titanium dioxide powder was suspended in distilled
35   water; hexachloroplatinic acid was added along with,
in certain cases, a sacrificial reducing ag nt. The
suspension was deaerated using N_2 gas and illuminated

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using a mercury lamp having illumination wavelengths
in the range of 240-400 nanometers to photod posit the
hexachloroplatinic acid on the titanium dioxide
powder. The resulting slurry was washed and dried at
5   room temperature to yield a platinized titanium
dioxide powder containing 1% platinum by weight. Sato
noted that in the absence of the sacrificial reducing
agent, the hexachloroplatinic acid disappeared from
the suspension either as a result of photoadsorption
10   or photodecomposition, but that, in any event, no
platinum was deposited unless a reducing agent was
added. For comparison, Sato also prepared a
platinized titanium dioxide catalyst made by reducing
hexachloroplatinic acid with a 0.1 M NaBH$_4$ solution in
15   0.1 N NaOH, and a catalyst prepared by the method of
Pichat.

        Whereas the exterior surfaces of powder grains
can be platinized to provide a catalytic surface, none
of the existing methods can successfully platinize
20   metal oxide materials other than powders. Existing
methods for preparing platinized catalysts have
various shortcomings that make them particularly
inappropriate or impractical for use with high surface
area, porous metal oxide materials. Although the
25   existing methods could be applied to such materials,
the expectation would be that the vast interior
surface area would not be adequately coated or that
the porous structure that ensures the high surface
area would be lost, or both. Therefore, it would also
30   be desirable to have a method for forming porous
ceramic metal oxide platinized catalysts that is both
cost-effective and compatible with high-surface area
materials.

                    Summary of the Invention
35   The present invention is summarized in that a
method for forming a platinized microporous metal

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oxide nanoparticulate ceramic catalyst employs as a
starting material a microporous, metal oxide,
nanoparticulate catalyst characterized as having
interconnected pores, a surface area greater than

5   about 50 m^2/g, and a mean pore diameter of less than
about 100 Å. A platinum precursor is adsorbed onto
the particles without photoillumination, for a time
sufficient to achieve adsorption equilibrium. A
platinum precursor is a platinum-containing compound

10   that can adsorb to the metal oxide material and can be
reduced to zero-valent platinum under reducing
conditions. For example, the $PtCl_6$ ionized form of
hexachloroplatinic acid is the preferred platinum
precursor in the present method.

15   Then, the microporous catalyst with the adsorbed
platinum precursor is subjected to reducing conditions
at a temperature that does not affect the mean pore
diameter of the micropores and at a pH that does not
dissolve the catalyst, until the platinum is reduced

20   to zero-valent platinum metal and so that a platinized
microporous metal oxide nanoparticulate ceramic
catalyst is formed.

          The platinized catalyst is then dried at a
temperature that does not affect the mean pore

25   diameter of the material.

          Materials prepared according to the method of the
present invention are physically distinct from
platinized powders and exhibit higher thermocatalytic
and photocatalytic turnover numbers than powders

30   prepared according to the same method. Moreover,
these platinized materials are able to readily degrade
and mineralize benzene, a difficult-to-degrade organic
compound, in the gas phase.

                    Detailed Description of the Invention

35   In a first aspect, the present invention is a
method for forming a platinized catalyst that solves

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the identified problems and shortcomings in the art.

The microporous nanoparticulate, metal oxide
ceramic starting materials for use in the
platinization method can be prepared in the manner
described in U.S. Patent No. 5,227,342 (Anderson and
Xu), which is incorporated herein by reference. See
also Xu, Q. and M. A. Anderson, J. Mater. Res. 6:1073
(1991) and Yamazaki-Nishida, S. et al., J. Photochem.
Photobiol., 70:95 (1993). Instead of using roto-
evaporation to prepare a xerogel, as has been
described, the materials were placed in a 55°C oven
for several days.

The nanoparticulate, microporous, metal oxide
particles produced in the methods therein described
are characterized by interconnected, rather than
closed, pores with a mean pore diameter of less than
100 Å and an available surface area in excess of about
50 m^2/g and as high as about 400 m^2/g. In mixed oxide
materials (e.g., mixed titania - zirconia or titania -
silica), higher surface areas, up to about 500 m^2/g,
can be achieved because pores can remain open longer
at higher temperatures during sintering. The surface
area is preferably 100-400 m^2/g. The mean pore
diameter, which represents an average of pores having
larger and smaller diameters, is preferably in the
range of 5 - 100 Å for catalytic reactions. It has
been determined by the inventors that the presence of
both very small platinized pores and somewhat larger
platinized pores in these materials is important to
their high activity. The larger pores capture
contaminants while the smaller pores trap and restrain
the contaminants in place until oxidation is complete.
The inventors refer to this phenomenon as "deep
oxidation catalysis." The porosity of these materials
is greater than about 30% and can range as high as
about 60%, depending upon the preparation conditions,
the firing temperature, and firing time. The metal

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oxide can be any transition metal that can be formed
into nanoparticulate ceramic materials, as well as
other elements such as silicon and aluminum. Although
titania is used in many of the examples below,

5   titania-based zirconia and silica mixed oxides are
also shown to function well. It is not thought that
the particular metal oxide selected is critical, but
rather that the nature of the microporous surfaces are
more responsible for the high quality of the

10   platinized materials. However, since titania is
recognized as having superior catalytic properties, it
is the preferred metal oxide. "Nanoparticulate" is
intended to indicate that the metal oxide materials
are formed in a sol-gel process in which discrete

15   metal oxide particles of irregular shape, sized, on
average, between about 3 and 50 nm, preferably 10-20
nm, in size, agglomerate in the manner described in US
Patent No. 5,227,342 to form particulate ceramic
materials (as opposed to polymeric materials). The

20   presence of pores in the described size range is
important for providing both high catalytic surface
area in large pores, as well as sites to trap
reactants in very small pores so deep oxidation
processes can occur. The porous metal oxide starting

25   materials can be in the shape of pellets, films,
sheets, membranes and the like. It is also possible
to coat and platinize these materials on support
surfaces having desired structures, such as honeycomb
structures. In this application, references to

30   "pellets" are intended to encompass nanoparticulate
materials in any physical form appropriate for use in
catalytic reactors. When the metal oxide is titanium
dioxide, as is preferred, the crystal structure of the
materials formed is primarily anatase (e.g., 89%

35   anatase, 11% rutile when fired at 300°C for four
hours), with the primary crystallites composing the
aggregated porous metal oxide materials having an

average size of about 80Å.

The metal oxide ceramic starting materials ar
platinized according to the following methods. If the
material is a solid membrane or an extruded product,
5   the material is crushed or ground into granular porous
pellets. Pellets are not intended to have a
particular shape, but are much larger than the grains
that comprise metal oxide powders. Granular pellets
between 0.05 and 10 mm in either dimension are
10   appropriate for use in the platinizing method herein
described. The pellets can be non-uniform in size and
shape. The pellets are size-screened by sieving and
are selected to meet the needs of the catalytic system
in which the pellets will be employed. A preferred
15   range of pellet dimensions is between 0.5 and 1.4 mm.

The pellets are immersed with stirring in an
excess of deionized water. The amount of water is not
critical. One hundred fifty ml of deionized water is
a suitable amount to accommodate 25 g of titanium
20   dioxide pellets although more or less water can be
used. The metal oxide particles should be suspended
in clear water. If the water turns a milky white
color when the pellets are added, the milky water
should repeatedly be decanted and replaced with fresh
25   deionized water until the deionized water remains
clear.

The platinum precursor is then added to the
immersed ceramic pellets. A convenient way to
introduce the platinum is to add an acid comprising
30   platinum and a halogen. Hexachloroplatinic acid
(H_2PtCl_6) is available commercially from Aldrich
Chemical as either a solid or as an 8% by weight
aqueous ionic solution, and is to be considered the
preferred acid. Either form of the acid can be used,
35   however the solid form hydrolyzes and dissolves too
rapidly in high humidity conditions to permit accurate
weighing. Thus, the most preferred form of

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hexachloroplatinic acid under standard open laboratory
conditions is the 8% by weight aqueous solution. The
appropriate amount of platinum is readily determined
from the molecular weights of the reactants. The
5   weight percent of platinum is determined relative to
the weight of the metal oxide. The platinum
preferably ranges as high as 2% by weight, but can be
higher. The amount of platinum need not be greater
than 0.5% by weight to prepare a platinized catalyst
10   having the desired activity, and can be less than 0.3%
or even 0.1% by weight. The intrinsic activity of the
platinized material (measured by turnover number) does
not increase after a loading level of about 0.5%.
However, the apparent activity of the material
15   (measured as extent of conversion per constant amount
of material) continues to increase up to about 2%.
Two percent platinum, by weight, is equivalent to 4.2%
by weight of the $PtCl_6$-ion platinum precursor. A 0.1
weight percent platinum deposit on titanium dioxide is
20   made by adding 0.263 ml of the 8% hexachloroplatinic
acid solution per gram of titanium dioxide.

When the hexachloroplatinic acid has been added
to the metal oxide catalyst, the two are allowed to
react for a period of about 20 minutes to 1 hour to
25   ensure adsorption equilibrium, at which time no
additional platinum ions adsorb to the metal oxide
material. Beyond about 1 hour, there is no additional
benefit observed from waiting a longer time.

The adsorption of the platinum to the metal oxide
30   pellets can be performed at room temperature and does
not require UV illumination. Nor is it necessary to
platinize under deaerated conditions, as has been
recommended in the platinization method of Sato, J.
Catal. 92:11-16 (1985).

35   At the end of the adsorption period, the
particles are allowed to settle and the water is
decanted from the reaction vessel.

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Next, the platinum ions are reduced to zero-
valent platinum metal. A preferred reduction method
uses sodium borohydride, NaBH$_4$, in dilute NaOH,
prepared fresh immediately before use. For
5   convenience, the reducing agent can be prepared during
the adsorption of the platinum to the metal oxide
pellets. The reducing agent can be present in
stoichiometric excess. The molar ratio of NaBH$_4$ to
platinum should be greater than 1. A concentration of
10   0.1-0.3 M NaBH$_4$ is suitable. Higher concentrations of
the reducing agent may be acceptable. The actual
concentration of sodium hydroxide is not absolutely
critical, although it must be sufficiently dilute
(about 0.05N-0.01N) so as not to attack and dissolve
15   the underlying metal oxide microporous particles. At
0.1N NaOH, dissolution of the metal oxide material is
observed. For each gram of 0.1% by weight
platinum/TiO$_2$ catalyst prepared, 2 ml of dilute NaOH
containing 0.02 g of sodium borohydride is suitable.
20   These amounts are adjusted accordingly for differing
amounts of platinized catalyst as well as for
variations in the weight percent of platinum loaded.

When the reducing agent is prepared, it is added
to the catalyst at room temperature. A large amount
25   of gas evolves during the reduction, so it is strongly
suggested that the addition be performed, with rapid
stirring, in an exhaust hood. After about 10 minutes
to one hour of rapid stirring, the liquid is decanted
and the platinized catalyst is washed with deionized
30   water several times until the NaBH$_4$ is removed. Four
washes are generally sufficient.

The platinized catalyst is then dried. It is
important not to dry the platinized catalyst at a
temperature that will increase the density and reduce
35   the porosity and mean pore diameter of the metal oxide
microporous platinized material. At temperatures
above about 400°C, marked reductions in mean pore

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diameter and porosity, and an increase in density, are
observed. Drying at about 60-120°C for 1-20 hours is
suitable.

     An alternate, but related, method for preparing

5   the platinized catalyst from metal oxide pellets is to
dry the pellets at a relatively low temperature (100-
120°C) for several hours, e.g. 3 hours. The 8%
hexachloroplatinic acid solution is added to the dried
particles at room temperature until the particles

10   become wet incipiently. After loading, the particle
are again dried under the same conditions as
previously. Then, the reducing agent in solution,
which is the same as in the previous method, is added
to the dried particles at room temperature. Then, the

15   liquid is decanted and the platinized particles are
rinsed and dried as previously. Platinized materials
prepared in this alternate method are comparable in
photocatalytic properties to those of the materials
that result from the preferred method.

20   The color of a platinized catalyst along a
spectrum ranging from light grey to dark black can
reflect the extent of platinum dispersion during
loading, with more thorough dispersion being reflected
in a uniformly darker color. It has been found that

25   the microporous nanoparticulate metal oxide ceramic
materials with adsorbed platinum ions can be reduced
in the gas phase at about 200°C with H_2 gas to obtain
platinized catalyst that is even darker and more
uniformly black than that which results from the $NaBH_4$

30   reduction, without apparent loss of internal pore
structure. This reduction temperature is also
significantly lower than that required by prior H_2
reduction methods, which, it is noted, are too high to
be used with the starting materials used herein. Even

35   more unexpectedly, the H_2 gas reduction can also be
performed at room temperature (about 20°-30°C) to
obtain platinized catalyst only slightly less black

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than those obtained at 200°C. However, materials
formed by hydrogen reduction are not as active as
those formed using $NaBH_4$-reduction, because the $NaBH_4$
reduction method may reduce only surface platinum from

5   valence state 6 to valence state 0, but might not
reduce the underlying bulk metal oxide toward the
zero-valent metal. In contrast, hydrogen reduction
also reduces the bulk metal oxide toward zero-valent
metal, which is black. However, the resulting metal

10   is not as catalytically active as platinum metal. As
a result, the black color of those materials formed by
hydrogen reduction does not correlate well with very
high activity.

        Economic considerations dictate that it is, of

15   course, preferred to minimize the amount of platinum
deposited, while still maintaining a suitably high
level of catalytic activity. Using these production
methods, platinized microporous metal oxide ceramic
materials containing up to 2 or 3 % by weight platinum

20   are preferably created, though it is more preferred
that the materials have less than 1% platinum, yet
more preferred for the materials to have between 0.1
and 0.6% platinum, and most preferred to have 0.3 -
0.5 % platinum by weight. Although a decrease in

25   platinum loading is understood to reflect economic
concerns, the art has heretofore been unable to
produce a material loaded with a small percentage of
platinum that achieves rapid and efficient catalysis
such as is described in the examples below. It has

30   been determined by the inventors that the catalytic
response of the platinized metal oxide microporous
materials reaches a plateau at about 0.3 - 0.5% by
weight platinum. As is shown below, in the examples,
it has also been determined that complete

35   mineralization of volatile aromatic compounds can
occur in a platinized microporous metal oxide
nanoparticulate catalyst at 0.1% by weight platinum.

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When the metal oxide pellets were titania, it was
noted that the pore size distributions of the
platinized materials were nearly identical to those
obtained for pure titania pellets, even at platinum
5   levels as high as 2 weight percent. The specific
surface areas of platinized titania particles were
about 160 m^2/g after firing at 300°C for four hours.
Transmission electron micrographs of these materials
magnified up to 330,000 times do not indicate the
10   presence of individual or aggregated platinum
particles on the titania particles at a platinum
loading of 0.3% by weight. Thus, for these
conditions, the platinum appears to be highly
dispersed over the surface of the titania catalyst.
15   This conclusion is supported by the physical
appearance of the platinized titania photocatalysts.
The catalyst platinized with less than 0.1% by weight
platinum is dark grey to black and varies from pellet
to pellet. As more platinum is placed on the titania
20   pellets, the number of grayish pellets decreases until
a uniform black coating is achieved in the 0.3 weight
percent platinum materials. As noted, the various
reduction methods each produce materials having
somewhat different blackness, although all of the
25   methods produce blacker materials than those produced
previously.

   Platinized catalysts prepared according to the
method of the present invention, as well as other
catalysts platinized in various ways have the
30   following characteristic colors, which can be
described by reference to standard a Pantone Color
Chart:

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Loading Weight % Platinum	Underlying Metal Oxide	Reduction Method	Pantone Color
0.5	Nanoparticulate Titania	$NaBH_4$	Process Black 2C
0.5	P25 Degussa Powder	$NaBH_4$	423C
0.5	Nanoparticulate Titania-Zirconia (12% Zirconia)		Process Black 2C[a]
2.5	Aldrich Titania Powder	Photo-reduction[b]	430C
0.3	Nanoparticulate Titania	$NaBH_4$	Process Black 2C
0.01	Nanoparticulate Titania	$NaBH_4$	400C, 401C, 402C, 406C, 407C, 408C
0.05	Nanoparticulate Titania	$NaBH_4$	408, 409[c]
0.1	Nanoparticulate Titania		425C

[a] Darker and shinier than Process Black 2C
[b] Prepared by National Renewable Energy Laboratory
[c] Particles of various colors

From these color data, it is apparent that at or below 0.05% Pt, there is insufficient Pt loaded onto the very-high surface nanoparticulate titania materials to cover all surface sites. Coverage is best at or above 0.1% Pt loading. It is also notable that examination in cross-section of the materials that appear to be fully black reveals that the black color is consistent even at the deepest interior portions of the material. Unplatinized nanoparticulate material is characterized as being eggshell white to light tan in color.

This method for platinizing incorporates improvements specific to its use with microporous

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pelletized granular starting material, rather than
the powdered starting material used by others.
Direct application of the Sato method to the starting
material used herein cannot achieve the desired
5   uniform coating or dark black color achieved by the
present inventors because the inner surfaces cannot
be treated. Nor can such high specific surface area
microporous materials be effectively coated in the
Sato method. Likewise when the present method for
10   platinizing is applied to standard titania powders
(Degussa P-25), the characteristic black color is not
observed and the catalytic activity is about two-fold
lower than that observed using the materials
disclosed herein.

15   As is shown in the non-limiting examples below,
these materials are above, upon exposure to UV light,
to achieve complete conversion and mineralization of
both aromatic and aliphatic compounds. In the
absence of UV light, these materials are sufficiently
20   thermocatalytic to achieve complete conversion of
organic material and mineralization of more than
about 75% of the organic material, even at
temperatures below 140°C. At higher temperatures,
better mineralization ratios are observed. The
25   striking ability of these catalysts to mineralize
organics, particularly aromatics, is believed to
result directly from the advantageous use of a
nanoparticulate, microporous metal oxide ceramic
material and from the invention of a preparation
30   method that takes advantage of the unexpected loading
properties of these materials. The method achieves
uniform dispersion throughout the entire porous
material while retaining high surface area and
porosity. Also, it appears that the platinum does
35   not aggregate on the catalyst surface as has been
observed in other materials, but rather is highly
dispersed.

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The truly dispersed platinum coating of
nanoparticulate materials is thought to develop
because of the distinct surface arrangement of these
materials compared to titania powder. Compared to
5   the size of the platinum metal, the substrate surface
of titania powder is very large. Individual platinum
metal ions can attach to the substrate in a widely
dispersed manner. However, because platinum is more
attracted to itself than to the titania substrate, it
10   tends to agglomerate with relatively vast uncoated
spaces. Uniform coating is approached only by adding
large amounts of platinum.

In contrast, the metal oxide starting materials
are nanoparticulate microporous materials sintered
15   into ceramic bodies as shown in Figs. 1-5 of U.S.
Patent 5,227,342, which are incorporated herein by
reference. Although these materials are solid
bodies, their characteristic particulate structure
reflects their formation from particulate sols. When
20   platinum ions adsorb to these materials, the actual
surface onto which platinum can migrate is small.
Said another way, even though these structure
materials have very high specific surface area, the
surface area of each discrete surface is quite small,
25   and is significantly smaller than a powder grain.
Accordingly, an adsorbed platinum can fill an entire
particle surface with very little material, yet the
adsorbed platinum is not free to migrate or
agglomerate because of the physical constraints of
30   the surfaces. This is true not only at the outer
particle surfaces, but also at the surfaces lining
the micropores within the nanoparticulate ceramic
materials. What results is a truly uniform
dispersion, despite very low platinum loading levels.
35   In contrast, when platinum can agglomerate, as on a
large uninterrupted powder grain surface, uniform
coating can only be achieved after sufficient

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platinum has been loaded that the surface becomes, in
effect, fully agglomerated. The lack of agglomerated
platinum can be observed visually by TEM where the
surface of the materials platinized according to the
5   method herein disclosed, even at a magnification of
330,000.

In addition, the nanoparticulate materials have
very high surface energy. In an effort to lower its
surface energy, these materials are receptive to
10   platinum binding.

The platinized microporous metal oxide materials
thus produced are unique among platinized catalysts
in that they couple a very high specific surface area
with a highly dispersed platinum coating throughout
15   the materials. Whereas titanium dioxide powders can
have a specific surface area of about 50 m^2/g, the
nanoparticulate microporous materials provide much
higher specific surface area both on their outer
surface and through their interior. It is
20   specifically because of these microporous inner
surfaces, however, that prior methods for making
platinized metal oxide catalysts are unsuitable for
platinizing these starting materials.

Since much of the specific surface area is
25   within the particles, rather than at the exterior
(visible) surface, platinization by
photoillumination, which reaches only the exterior
surface and areas just below the exterior surface, is
less efficient than the non-photoilluminating method
30   described herein and, in fact, can never platinize
the deep interior surfaces. Moreover, prior methods
for platinizing at high temperatures are also not
useful with the high specific surface area platinized
catalyst of the present invention.

35   The platinized catalysts formed in the method
are more desirable than existing platinized powders
because the powdered materials cannot be used

effectively for gas-solid phase reactions conducted
in a fixed bed reactor. Powders are generally used
only to produce a slurry in a liquid phase reaction
or are trapped on a support in a gas phase reaction.
5   But there is simply insufficient catalytic surface
area on powders to achieve acceptable results. The
combination of the reduced platinum load coupled with
the high dispersion, the variety of pore sizes, and
very high catalytic surface area of the platinized
10   microporous materials make the products of the
described method particularly advantageous for
remediation of contaminating materials in the gaseous
state. As is demonstrated below in the examples,
these materials can readily mineralize organic
15   contaminants that are generally recognized as
extremely difficult to mineralize. In addition,
these materials find utility as cracking catalysts,
or other applications that do not require complete
mineralization.
20   The platinized materials can be used in a fixed
bed photoreactor as is described herein in the
Examples. Alternatively, these materials can also be
advantageously employed in any catalytic reactor
adapted for degradation of gaseous material.
25   Conditions for complete degradation of benzene are
provided herein. One of ordinary skill will
appreciate that the particular conditions appropriate
for mineralizing other aromatic or complex aliphatic
volatile compounds can be determined experimentally.
30   The important conditions generally include space time
(which itself depends upon reactor size and shape),
water vapor and oxygen requirements, VOC
concentration and catalyst amount.
           The present invention is further clarified by
35   consideration of the following examples which are
intended to be exemplary rather than limiting.

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EXAMPLE 1

Catalyst Preparation

Titanium dioxide particles were prepared by a
sol- gel technique as previously described in U.S.
Patent No. 5,227,342. Titanium tetraisopropoxide was
hydrolyzed under acidic conditions and the resulting
colloidal suspension was then dialyzed until the pH
of the suspension was about 4. The suspended
colloidal particles were between about 10 and 20 nm
in size. The dialyzed sol was evaporated to form a
xerogel which was heated under controlled conditions
to form a microporous ceramic material. The ceramic
material was then ground and sieved to obtain
titanium dioxide pellets having diameters between 0.5
and 1.4 mm.

        BET analysis of nitrogen sorption data for these
pellets revealed typical specific surface areas of
170 m²/g and porosities of 55%, when the ceramic
materials were fired at 300°C for 4 hours. The mean
pore diameter for these materials was about 45 Å. X-
ray diffraction analysis indicated that the crystal
structure of these materials was 89% anatase and 11%
rutile with the primary crystallites having an
average size of about 80 Å.

        The titania pellets were placed in water and
were then impregnated with a dilute solution (8% by
weight) of aqueous hexachloroplatinic acid (Aldrich
Chemical, Catalog No. 26258-7). Sufficient platinum
was used to achieve platinum loading of between 0.1%
and 2% platinum by weight relative to the titania
pellets. The adsorbed platinum was then directly
reduced with a solution 0.3 M NaBH₄ in 0.01 M NaOH at
room temperature. Finally, the pellets were dried at
105-110°C for 2 hours.

        BET analysis demonstrated that the pore size
dimensions of these platinized pellets (with up to 2%
by weight platinum) were identical to those obtained

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for pure titania. The specific surface area of the
platinized titania pellets was about 160 m^2/g, not
appreciably different from the pure titania
particles. Transmission electron microscopy (TEM),
5   up to a magnification of 330,000, did not indicate
the presence of individual platinum particles on the
titania at a platinum loading of 0.3 weight percent.
At 0.1 weight percent platinum, the catalytic
material ranges from dark grey to black and varies
10   from particle to particle, as reported elsewhere in
the specification. However, at higher platinum
loads, the number of grayish particles decreases
until a uniform black coating is achieved at 0.3
weight percent platinum.

15   EXAMPLE 2
Experiments to determine the photocatalytic
activities of the platinized materials (and their
unplatinized counterparts) were conducted in a fixed
bed annular photoreactor operated in a single-pass
20   mode. This annular reactor was fabricated from
glass, with the width of the annulus being 2-3 mm.
The annulus surrounded a 4 W fluorescent black light
bulb (GE F4T5-BLB) positioned along the longitudinal
axis of the reactor. This bulb emits radiation over
25   the range of 300-425 nm, with peak intensity centered
at 350 nm. This reactor design was employed because
it provides efficient utilization of that portion of
the incident radiation that strikes the
photocatalyst, and because it allows a relatively
30   large amount of catalyst to be placed in the reactor.
The illuminated catalyst is not confined to the inner
surface of the annulus. Because of the irregular
particle shapes, annular radiation sometimes does not
strike the catalyst until near the outer surface of
35   the annulus. There are even gaps where radiation can
pass through the annular reactor. Accordingly, a

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layer of aluminum foil was wrapper around the reactor
to reflect some of this radiation back into the
reactor. Thus, the photoactive catalyst is actually
spread throughout the reactor, although the largest

5   proportion of photoactive catalyst was located at the
inner region of the annulus. The irregular
distribution of photoactive catalyst increases the
probability that a reactant gas will contact a
photoactive surface at some time during its flow

10   through the reactor.
     Each experiment employed 19 g of platinized
catalyst prepared accordingly to the method of the
present invention (0.1% platinum by weight) unless
otherwise noted. However, given the non-uniform

15   sizes and shapes of the photocatalyst particles,
these particles were not closely packed into the
annular region of the reactor. Thus, the
distribution of the catalyst within the annulus was
not uniform. In addition, these materials display a

20   high absorptivity for near-UV radiation with an
energy above the band gap energy of the material. It
is likely that the photoactive region of the catalyst
is only a layer of about 10 microns thick at the
surface of the illuminated portion of the catalyst.

25   As a result, it is not possible to accurately
estimate the amount of catalyst that is actively
illuminated. Most of the photocatalyst is probably
not illuminated, especially that portion that resides
deep in the interior of the porous pellets.

30   The reactant gas, typically benzene, was
delivered to the apparatus from a compressed gas
cylinder in a feed stream that also included
hydrocarbon-free air (less than 0.1 ppm total
hydrocarbons, available from Scott Specialty Gases),

35   zero air (21% oxygen, 79% nitrogen, available from
Liquid Carbonic), oxygen (99.999%, Liquid Carbonic)
and nitrogen (99.999%, Liquid Carbonic). The benzene

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concentration was 491 ppmv $\pm$ 2%. The gas feed stream
was humidified by passage through a water saturator,
and the water content in the reactant stream was
fixed by controlling the flow rate and the

5   temperature of the saturator. The mole fractions of
the gaseous mixture of benzene, oxygen and water
vapor were 4.9×10^{-4}, 0.2, and 0.03, respectively.
At a significantly lower water mole fraction, <5 ppm,
conversion using the unplatinized catalyst was still

10   shown to be substantially complete (at 130°C), but
the mineralization ratio (moles of CO_2 produced per
mole of input organic material converted) was in
steep and rapid decline to about 3, although this
could be increased to about 4, upon addition of water

15   to the 0.03 mole fraction level. At a water mole
fraction of 0.015, conversion and mineralization can
be achieved. Reactor temperature was varied using
heating tapes and a temperature controller (Glas Col
D.T. II). The reactor was operated by starting

20   illumination when the gas flow was started. No
measurements were taken during the first 15 minutes
of flow to allow the system to reach thermal
equilibrium with the heat energy produced by the UV
bulb.

25   The product stream was allowed to flow
continuously from the reactor to the sampling loop of
a chromatographic valve. A Hewlett-Packard 5890 gas
chromatograph (Series II) equipped with a flame
ionization detector (FID), a thermal conductivity

30   detector (TCD) and a Porapak R column was employed to
analyze discrete samples of the reactor effluent
stream. Benzene and carbon dioxide concentrations
were determined by FID and TCD, respectively. The GC
was calibrated using known concentrations of benzene

35   and carbon dioxide.
          During the experiments described herein, the
only carbon-containing species in the product stream

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that were observed at concentrations large enough to
be quantified were benzene and carbon dioxide. Other
extremely small peaks were observed intermittently at
concentrations below 1 ppmv, assuming an identical
5   sensitivity of the FID for these species and benzene.
Since these peaks were not observed consistently even
during the performance of a single experiment, no
effort was made to identify them.

EXAMPLE 3

10   Photocatalytic Decomposition of Benzene
                   Over Platinized Catalyst
         Using the input gas stream described above, the
platinized catalysts were evaluated under steady
state conditions. Steady state conditions were
15   reached after 2 to 3 hours of UV photoillumination
when the platinized titania catalyst was used. At
least five hours were required to achieve a steady
state using the unplatinized microporous titania
membranes tested for comparison. At steady state,
20   conversion on the unplatinized catalyst remains
constant, although a gradual decrease in
mineralization ratio is observed over time. This is
thought to result from adsorption of some species to
the catalyst that correlates with a yellowing of the
25   unplatinized catalyst. Because of the dark color of
the platinized catalyst, the presence of yellowing
cannot be confirmed.
         Essentially complete conversion (degradation) of
benzene was obtained with the photoilluminated
30   platinized catalyst at all operating temperatures in
the measured range of 70°C to 140°C. The smallest
mineralization ratio obtained with the platinized
catalyst was 5.1, observed at 70°C. The highest
mineralization ratio, 5.8, was obtained at
35   temperatures of 110°C and higher. The difference in
mineralization ratio between 5.8 and the

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stoichiometric value of 6 can be ascribed to analytical errors in measuring the concentrations of the reactants in products as well as to possible adsorption of carbon on the surface of the platinized

5   catalyst.

       These results contrast with those obtained using the unplatinized titania starting material as the photocatalyst. Using that material, the mineralization ratio appears to be somewhat dependent

10   upon temperature, increasing from about 3.6 to about 4.3 between the temperatures of 70°C and 140°C. Likewise, the photocatalytic conversion or degradation of benzene increases from about 60% to about 80% between 70°C and 110°C, then tapers off in

15   slope to a maximum conversion of about 86% at 140°C.

       Using the platinized catalyst at a reaction temperature as low as 70°C and a space time as low as 1.8×10^9 g-seconds per mole in the annular reactor containing catalyst pellets, the conversion of

20   benzene was 100% and the mineralization ratio (moles of carbon dioxide produced relative to moles of benzene converted) was above 5.0. The mineralization ratio approached the theoretical maximum of 6.0, if either the reaction temperature was increased to

25   110°C or if the space time was increased to greater than 4×10^9 g-seconds per mol. By comparison, the unplatinized titania catalyst at 130°C can achieve full conversion only at space times higher than 2.2×10^9. At that condition, however, the mineralization

30   ratio is near a plateau of less than 4.4.

                            EXAMPLE 4
             Effect of Oxygen on Conversion and Mineralization
                    Using Platinized Titania Catalyst
             The effect of oxygen on both conversion and

35   mineralization of benzene was determined by

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performing the photocatalytic reaction at various
mole fractions of oxygen between 0.1 and 0.6 on 0.1
weight percent platinum titania catalyst at 70°C.
The mole fractions of benzene and water vapor were

5   2.5 x 10^{-4} and 1.5 x
10^{-2}, respectively. The space time was 1.9 x 10^9
gram-seconds per mol. The results indicated that
conversion is sensitive to the concentration of
oxygen only when the mole fraction of oxygen in the

10   gaseous reactant stream is lower than 0.2. At higher
than 0.2 mole fraction, conversion is essentially
100%. However, the mineralization ratio clearly
increases as the mole fraction of oxygen increases up
to a mole fraction of 0.4. The optimum mole fraction

15   of oxygen for the mineralization of benzene to carbon
dioxide was between about 0.4 and 0.55, with a
maximum at about 0.45. The reason for the observed
decrease in mineralization ratio at mole fractions of
oxygen greater than 0.55 is not known.

20   EXAMPLE 5
          Comparative Thermal Catalytic Oxidation of Benzene
               A series of experiments were performed to
       directly compare the thermal catalytic activity of
       platinized titania catalysts prepared in accordance

25   with the present method against other platinized
       catalytic material. Catalyst was placed in a tubular
       reactor surrounded by four 4W UV lights (GE). The
       tubular reactor was coated with foil so that only
       thermal, but not light effects were measured. In

30   these experiments, which are intended only as
       demonstrations of the superiority of the claimed
       materials, starting materials and reduction
       conditions were compared directly. Results are
       reported in Table 1.

35   Platinized titania pellets, at 0.3% and 0.5% by
       weight platinum, were prepared according to the

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sodium borohydride reduction method of the pr sent
invention. In addition, Degussa P25 powder was
compressed into pellets comparable in size to those
of the starting materials of the present method, and

5   were either platinized to 0.5 weight percent using
NaBH₄ reduction, or were platinized to 0.3 weight
percent by H₂ reduction at 200°C. Finally, mixed
titania-zirconia and titania-silica pellets were
platinized to 0.5 weight percent platinum according

10   to the method of the present invention. The mixed
oxide starting materials were prepared according to
the modified method of Anderson and Xu. Separate Zr
and Ti sols were prepared and then mixed together.
The mixed sol, formed of separate Zr and Ti

15   particles, was not roto-evaporated, but was dried in
an oven as described above. The xerogel thus formed
was fired to form a mixed oxide ceramic material
which was crushed and platinized as described herein.
The resulting material had a mean pore diameter of

20   35Å. Also used in these experiments was commercially
available 5894 industrial grade thermal catalyst
(Union Carbide).

The following conditions were employed.
Benzene, at a concentration of 509 ppm was introduced

25   into the tubular reactor with oxygen gas at a molar
ratio of 0.2, the remainder being nitrogen, water
vapor being present at less than 5 ppm. The feed
stream flow rate was 20 ml/minute. The weight of
each catalyst tested was 0.407 g. Unless otherwise

30   noted, the reaction time was about 20 hours.

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TABLE 1

Catalyst	Reduction Method	CO$_2$ Production Rate (mol CO$_2$/s·gPt)	[CO$_2$] Produced	Apparent Turnover Number (mol C$_6$H$_6$/s·gPt)
0.3% wt Pt/TiO$_2$	NaBH$_4$	2.6 x 10^{-6}	238 ppm	5.2 x 10^{-7}
0.5% wt Pt/TiO$_2$	NaBH$_4$	2.4 x 10^{-6}	357 ppm	4.9 x 10^{-7}
0.3% wt Pt/P-25	H$_2$ at 200°C	0	0	0
0.5% wt Pt/P-25	NaBH$_4$	8.5 x 10^{-7}	127 ppm	2.6 x 10^{-7}
0.5% wt Pt/TiO$_2$-ZrO$_2$	NaBH$_4$	2.6 x 10^{-6}	386 ppm	5.3 x 10^{-7}

The conversion percent and mineralization ratio
for catalytic oxidation of benzene were also
determined for various platinized catalysts. Table 2
demonstrates the clear superiority of catalysts
prepared on microporous, nanoparticulate substrates as
opposed to other commercial platinized catalysts.
Note that these reactions were not intended to
represent optimal oxidation conditions, but rather to
provide a rapid comparison of various catalysts.
Accordingly, the reactions were run for a short time,
at a high flow rate using a small amount of catalyst.
Therefore, these reactions were not run under
conditions where one would expect complete conversion;
yet, under these conditions the materials of the
present invention exhibit mineralization ratios
between 5 and 6, reflecting almost complete
mineralization of the converted benzene. Under more
typical reaction conditions, complete mineralization
and conversion would therefore be expected.

TABLE 2

Catalyst	Reduction Method	Conversion (percent)	Mineralization ratio
0.3% wt Pt/TiO$_2$	NaBH$_4$	9.1	5.2
0.5% wt Pt/TiO$_2$	NaBH$_4$	14.5	4.9
0.5% wt Pt/TiO$_2$-ZrO$_2$	NaBH$_4$	15.4	4.9
0.5% wt Pt/TiO$_2$ (P-25)	NaBH$_4$	7.5	3.4
0.3% wt Pt/P-25	H$_2$ gas at 200°C	0	--
5894-Industrial (.16%Pt)	unknown	0	--

Th rmocatalytic oxidation of ethylene was also
monitored using the various catalysts. In this

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experiment, reported in Table 3, oxygen was pres nt in the feed stream at 0.045 molar ratio, ethylene gas was present at the indicated concentration, the flow rate was 60 ml/minute and water vapor was present at less

5   than 5 ppm. The temperature was 105-106°C and 0.41 g of each catalyst was tested. Markedly better catalytic activity was observed using the materials of the present invention. With these materials, at 105°C, 50% conversion of ethylene or greater,

10   preferably 75% conversion or greater, and most preferably 90% conversion or greater is expected. Likewise, apparent turnover numbers of 10^{-5} or higher for ethylene are also characteristic. Comparable results will be observed at other temperatures.

15

TABLE 3

Catalyst	Reduction Method	C_2H_4 (ppm)	Conversion (percent)	Apparent Turnover Number
0.3% wt Pt/P-25	H_2 gas at 200°C	389	1.3	1.7×10^{-7}
0.3% wt Pt/TiO$_2$	NaBH$_4$	391	99.4	1.3×10^{-5}
5894-Industrial (.16%Pt)	unknown	381	6.9	1.6×10^{-6}

The data of the preceding tables demonstrates the superior ability of the materials prepared in accordance with the present invention to convert and

25   mineralize organic materials. It further demonstrates the superior turnover rates that these materials provide. Also shown is the unexpectedly good results observed when the method of the present invention is applied to nanoparticulate microporous starting

30   materials, as well as the fact that when other starting materials are used in the present method, the platinized materials obtained are about 50% less catalytically active.

EXAMPLE 6

35   Catalytic Properties of Platinized Nanoparticulate Microporous Ceramic Materials

Platinized and unplatinized materials prepared according to the method of the present invention were evaluated separately both in terms of conversion and

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mineralization under photothermocatalytic and
catalytic conditions using the annular reactor.

With respect to the unplatinized titania
catalysts, conversion of benzene is about 60% lower in
5   the absence of UV illumination across the temperature
range 70-140°C. At its maximum, the unplatinized
material exhibits about 25% conversion at 140°C.
However, across the entire temperature range, the
mineralization ratio of the unplatinized material is
10   constant at less than 1.5.

In striking contrast, however, the applicants
have here determined that the platinized catalyst
prepared according to the method of the present
invention is very catalytic. In the complete absence
15   of UV illumination, these materials (0.1%wt Pt)
exhibit complete conversion of benzene at temperatures
as low as 130°C. Moreover, a sharp upward-rising
slope is observed in the temperature range between 90
and 130°C. Over this interval, conversion increases
20   from about 10% to 100%. Likewise, over this same
temperature range, the mineralization of benzene
increases from a ratio of about 1 at 90°C to greater
than 4.5 at 130°C. It is concluded from these
observations that platinizing the titania catalyst
25   promotes both the photocatalytic and thermocatalytic
reactions. Moreover, the ability to complete convert
benzene and to achieve almost complete mineralization
at temperatures below 140°C is believed to be unique
among platinized catalysts. Typically, catalytic
30   converters operate with maximal efficiency at higher
temperatures such as 200°C to 600°C, depending upon
the chlorination of the compounds converted. What
these platinized materials offer, then, is an
opportunity to provide efficient catalytic conversion
35   at lower temperatures, thereby permitting the
conversion of toxic emissions from vehicles, such as
automobiles and trucks, at temperatures where no such

conversion can now take place using existing catalytic
converters. This observation can translate directly
into reduced toxic emissions.

It is also noteworthy that since these catalytic
5   materials can be made to operate with almost equal
efficiency in the presence or absence of UV
photoillumination, a significant cost reduction can be
obtained by eliminating the need for photoillumination
entirely, relying exclusively on thermocatalysis for
10   conversion and mineralization of toxic materials such
as benzene. This is particularly attractive, since
uniform temperature control can readily maintain the
catalytic material at a uniform temperature, thus
allowing catalytic activity throughout the microporous
15   materials. In contrast, it has already been noted
that photoillumination of these materials is
necessarily less than 100% efficient since UV
illumination cannot pass entirely into the interior of
the pelletized ceramic bodies.

20   Complete conversion or mineralization is not
required of a process using the disclosed platinized
materials. The materials themselves are capable of
promoting both high conversion and high mineralization
rates. However, in any particular application, even
25   partial conversion or mineralization may be
sufficient, particularly when toxic intermediates are
not produced or are produced in small amounts as
products of conversion. Moreover, for certain
materials even moderate conversion and mineralization
30   can represent dramatic improvement over prior
catalytic processes. In such cases, the improved
activity of the disclosed materials is itself
sufficient to merit their use in such remedial
processes.

35   These platinized materials have been successfully
used at 70°C to completely mineralize xylene (100 ppm
in the feed stream) and methylene chloride (100 ppm in

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the feed stream), in addition to the other compounds
described herein.

　　　The present invention is not intended to be
limited to the embodiments described in the examples,
but rather to encompass all such modifications and
variations as come within the scope of the following
claims.

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CLAIMS

1.   A method for forming a platinized
microporous metal oxide ceramic catalyst, the method
comprising the steps of:
5   providing a microporous nanoparticulate ceramic
metal oxide material having micropores in the interior
thereof with a mean pore diameter of less than 100 Å,
the material having an available surface area of
between 50 and 500 m^2/g;
10   adsorbing a platinum precursor onto the
microporous material without photo-illumination, at a
temperature between room temperature and 200°C for a
time sufficient to achieve steady-state adsorption of
the platinum precursor;
15   reducing the adsorbed platinum precursor to zero
valent platinum metal on the microporous material at a
temperature that does not affect the mean pore
diameter of the microporous material and at a pH that
does not dissolve the microporous material; and
20   drying the platinized microporous material at a
temperature that does not affect the mean pore
diameter of the material to form a platinized
microporous metal oxide catalyst.

2.   A method as claimed in Claim 1 wherein the
25   catalyst is capable, under photoillumination at a
temperature of 70°C, of complete conversion of an
input stream of benzene gas, with a mineralization
ratio of greater than 5.

3.   A method as claimed in Claim 1 wherein the
30   catalyst can achieve, at a temperature of 105°C,
greater than 50% conversion of ethylene with an
apparent turnover number of 10^{-5} or greater.

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        4.   A method as claimed in Claim 1 wherein the
adsorbing step comprises mixing the microporous
material with hexachloroplatinic acid for less than
about one hour at room temperature.

5   5.   A method as claimed in Claim 1 wherein the
reducing step comprises soaking the platinum-adsorbed
material in a basic solution comprising 0.1 - 0.3 M
sodium borohydride at room temperature.

        6.   A method as claimed in Claim 1 wherein the
10   reducing step comprises exposing the platinum-adsorbed
material to H_2 gas at a temperature between room
temperature and about 200°C.

        7.   A method as claimed in Claim 1 wherein the
microporous material is titania having dimensions
15   ranging in size from 0.05 mm to 10 mm.

        8.   A platinized catalyst comprising:
        a microporous nanoparticulate ceramic metal oxide
material having micropores in the interior thereof
with a mean pore diameter of less than 100 Å, the
20   material having an available surface area of between
50 and 500 m^2/g; and
        a platinum coating uniformly dispersed on the
available surface area.

9.   A platinized catalyst as claimed in Claim 8
wher in the catalyst can achieve, under
photoillumination at a temperature of 70°C, complete
conversion of an input stream of benzene gas, with a
5   mineralization ratio of greater than 5.

10.   A platinized catalyst as claimed in Claim 8
wherein the catalyst can achieve, without
photoillumination at a temperature below 140°C,
complete conversion of an input stream of benzene gas,
10   with a mineralization ratio of greater than 4.5.

11.   A platinized catalyst as claimed in Claim 8
wherein the catalyst can achieve, at a temperature of
105°C, greater than 50% conversion of ethylene with an
apparent turnover number of 10^{-5} or greater.

15   12.   A platinized catalyst as claimed in Claim 8
wherein the platinum comprises less than 0.6% by
weight of the weight of the metal oxide.

13.   A platinized catalyst as claimed in Claim 8
wherein the platinum comprises between 0.1% and 0.3%
20   by weight of the weight of the metal oxide.

14.   A method for remediating an organic compound
in the gas phase without photoillumination, the method
comprising the steps of:
        providing a microporous nanoparticulate ceramic
25   metal oxide material having micropores in the interior
thereof with a mean pore diameter of less than 100 Å,
the material having an available surface area of
betw en 50 and 500 m²/g;

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adsorbing a platinum precursor onto the
microporous material without photo-illumination, at a
temperature between room temperature and 200°C for a
time sufficient to achieve steady-state adsorption of
5   the platinum precursor;
reducing the adsorbed platinum precursor to zero
valent platinum metal on the material at a temperature
that does not affect the mean pore diameter of the
microporous material and at a pH that does not
10   dissolve the microporous material;
drying the platinized microporous material at a
temperature that does not affect the mean pore
diameter of the material to form a platinized
microporous metal oxide catalyst; and
15   exposing the catalyst to an input stream of the
organic compound in the gas phase at a temperature and
for a time sufficient to completely convert the
organic compound and to achieve at least about 75%
mineralization.

20   15. A method as claimed in Claim 14 wherein the
catalyst is exposed to the input stream without
photoillumination.

16. A method as claimed in Claim 14 wherein the
catalyst is exposed to the input stream at a
25   temperature below 140°C.

17. A method as claimed in Claim 14 wherein the
catalyst is capable, without photoillumination at a
temperature below 140°C, of complete conversion of an
input stream of benzene gas, with a mineralization
30   ratio of greater than 4.5

18.   A method as claimed in Claim 14 wherein the
catalyst is capable, under photoillumination at a
temperature of 70°C, of complete conversion of an
input stream of benzene gas, with a mineralization
5   ratio of greater than 5.

19.   A method as claimed in Claim 14 wherein the
catalyst can achieve, at a temperature of 105°C,
greater than 50% conversion of ethylene with an
apparent turnover number of 10^{-5} or greater.

INTERNATIONAL SEARCH REPORT	International application No.
	PCT/US96/08471

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6)   :B01J 23/00, 23/40; C07B 63/00
US CL   :502/325, 326, 349, 350; 204/158.21
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. :   502/325, 326, 349, 350; 204/158.21, 158.2; 423/437R

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP, A, 633064-A1 (MURASAWA ET AL) 11 January 1995, page 4, lines 22-39.	1-13
Y	WO, A, 92/08544 (YUE ET AL) 11 December 1991, page 6, lines 18-26; page 7, lines 4-7.	1-13
Y	Journal De Chimie, volume 5, No. 12-1981, 07 August 1981, Pichat et al, "Photocatalytic Hydrogen Production From Aliphatic Alcohols over a Bifunctional Platinum on Titatinum Dioxide Catalyst", pages 627-636, especially page 628.	1-13
Y	Journal of Catalysis 92, 11-16, 25 April 1984, S. Sato, "Photoelectrochemical Preparation of Pt/TiO2 Catalysts", pages 11-16, especially page 13.	1-13

[X] Further documents are listed in the continuation of Box C.	[ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
06 AUGUST 1996	**30 SEP 1996**

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,449,443 (JACOBY ET AL) 12 September 1995, column 3, lines 40-68; column 4, lines 57-64.	14-19
Y	US, A, 5,032,241 (ROBERTSON ET AL) 16 July 1991, column 1, lines 8-40.	14-19
Y	US, A, 5,252,190 (SEKIGUCHI ET AL) 12 October 1993, column 1, line 25; column 2, lines 49-55; column 4, lines 31-33	14-19